U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-296 089

Nonmethane Organic Emissions from Bread Producing Operations

Midwest Research Inst, Kansas City, MO

Prepared for

Environmental Protection Agency, Research Triangle Park, NC Office of Air Quality Planning and Standards

Dec 78

PB 296089

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-79-001
December 1978

Air

EPA

Nonmethane Organic Emissions from Bread Producing Operations

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

PB296089

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-450/4-79-001		

4. TITLE AND SUBTITLE	5. REPORT DATE
Nonmethane Organic Emissions From Bread Producing Operations	December 1978
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Ralph M. Keller	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Midwest Research Institute 425 Volker Boulevard Kansas City, MO 64110	2AA635
	11. CONTRACT/GRANT NO.
	68-02-2524
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

EPA Project Officer: Tom F. Lahre

16. ABSTRACT

A laboratory testing program is described wherein ethanol emissions were measured from the various operations involved in bread production. The approach involved monitoring, via a flame ionization detector, ethanol given off during the mixing, rising, and baking steps in the making of bread. Both the straight-dough and sponge-dough processes were evaluated. Emission factors are developed in terms of quantity of ethanol emitted per quantity of bread produced. No tests were made at an actual bakery to confirm the emission factors determined in these laboratory tests; however, the values determined compare reasonably well with theoretically determined values.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Bakery Baking Bread Dough Emissions Ethanol Ethyl Alcohol Evaporative Emissions Volatile Organic Emissions		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	53
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	PC F04/MF F01

EPA Form 2220-1 (9-73)

EPA-450/4-79-001

Nonmethane Organic Emissions from Bread Producing Operations

by

Ralph M. Keller

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Contract No. 68-02-2524

EPA Project Officer: Thomas F. Lahre

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1978

ja

This report is issued by the U. S. Environmental Protection Agency to provide technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations in limited quantities from the Library Services Office (MD-35), U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110, in fulfillment of a contract. The contents of this report are reproduced herein as received from Midwest Research Institute. The opinions, findings and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered an endorsement by the Environmental Protection Agency.

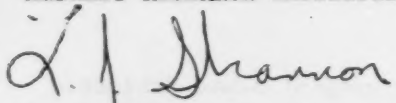
Publication No. EPA-450/4-79-001

PREFACE

This report was prepared for the Environmental Protection Agency (Mr. Thomas F. Lahre, Project Officer) to summarize results of laboratory experiments carried out under Work Assignment 4 of Contract No. 68-02-2524. The work was performed in the Environmental and Materials Sciences Division of Midwest Research Institute under the supervision of Dr. Chatten Cowherd, Head, Air Quality Assessment Section. Dr. Ralph Keller was the project leader and the author of this report.

Approved for:

MIDWEST RESEARCH INSTITUTE



L. J. Shannon, Director
Environmental and Materials
Sciences Division

December 22, 1978

SUMMARY

Two experiments were conducted to measure the emissions of total non-methane organics during the production of bread. One experiment determined the emissions during the production of bread by the straight dough process. The other experiment measured emissions during production by the sponge-dough process. Measurement of the emissions was performed with a gas chromatograph.

Ninety-five percent of the emissions from the processes was found to be ethanol and the remaining 5% consisted of three other organic compounds. The straight dough process emitted 0.5 g ethanol per 1 kg of bread produced. Emissions from the sponge-dough process were 4.6 g ethanol per 1 kg of bread produced. In both processes, emissions released during baking comprised the majority of the total emissions. Negligible amounts of ethanol remained in the bread after baking.

These values are low compared to the value of 8 g/kg of bread estimated through theoretical considerations. One factor affecting this is the difference in sweetener concentration between the experimental and theoretical cases. In these experiments, the sweetener concentrations were approximately 5%, while the theoretical analysis assumed a sweetener concentration of 10%. Adjusting for the sweetener concentration results in more comparative values between experimental and theoretical emission rates.

TABLE OF CONTENTS

Preface iii
Summary iv
Figures vi
Tables vi

1. Introduction 1
2. Breadmaking Processes 2
3. Experimental Apparatus and Procedure 4
4. Experimental Data 7
   Straight Dough Process 7
   Sponge-Dough Process 11
5. Discussion 15
6. Recommendations 16

References 17
Appendices

A. Commercial Bakeries as a Major Source of Reactive Volatile Organic Gases 18
B. Sample Calculations 37
C. Raw Data For the Two Experiments 42

FIGURES

Number		Page
1	Experimental Apparatus.	5
2	Ethanol Emission Rate	10
3	Dilution System	12
4	Ethanol Emission Rate	14

TABLES

Number		Page
1	Straight Dough and Sponge-Dough Formulations.	3
2	Ingredients and Procedure for Straight Dough Process. . .	7
3	Statistics for the Breadmaking Experiment - Straight Dough Process	9
4	Ingredients and Procedures for the Sponge-Dough Process .	12
5	Statistics for the Breadmaking Experiment - Sponge-Dough Process	13

SECTION 1

INTRODUCTION

Within the last year, it has been proposed by Mr. David C. Henderson of the U.S. Environmental Protection Agency (EPA) Region IX, that the production of certain bakery products entails nonmethane organic emissions. Mr. Henderson became aware of the production of ethanol by yeast in bakery dough as the dough was leavened and investigated the possibility of the ethanol escaping from the dough into the atmosphere. He focused his attention primarily on bread dough although all yeast leavened dough is capable of emitting ethanol. A paper detailing his investigation is included in Appendix A.

Because Mr. Henderson's data suggested that large bakeries could be potentially significant sources, an experimental program was initiated to measure the nonmethane organic emissions from the various processing stages of breadmaking. The program was designed to measure emission rates for total nonmethane organic compounds in the production of bread. Experiments were conducted to measure emissions from the two common dough processes. On August 4, 1977, experiments were performed with bread produced by the straight dough process, and on November 15, 1977, experiments were performed with bread produced by the sponge-dough process (see Section 2 for a description of these processes).

The following sections of this report discuss the breadmaking processes, experimental apparatus, data acquired, implications of the data, and recommendation for future investigation.

SECTION 2

BREADMAKING PROCESSES

One essential step in the production of bakery products is the leavening of dough to a desired volume by the production of carbon dioxide (CO_2) within the dough. The production of CO_2 may be by chemical or biological means. The bakery processes which use biological leavening produce ethanol as a by-product of leavening and are of interest in this report.

The biological production of CO_2 within bread dough requires the use of yeast and sucrose (sweetener). The yeast is a fungus which metabolizes the sucrose through a series of chemical stages to the end products of CO_2 and ethanol (ethyl alcohol). The CO_2 leavens the dough while the ethanol evaporates.

A brief discussion of the chemistry of breadmaking may be found in Mr. Henderson's paper in Appendix A. The chemical reactions and stages are shown as well as a theoretical estimate of the quantity of ethanol created in the leavening process.

Bread is generally produced by two methods: one is the straight dough process, the other is the sponge-dough process. In the straight dough process, all ingredients are mixed into the dough in a single-step procedure. This method is used most often in home baking and to some degree in commercial baking. The sponge-dough process requires that part of the ingredients be mixed and allowed to ferment for 3.5 to 5 hr, after which the rest of the ingredients are added. This process is used most often by commercial bakeries. A listing of the ingredients and their portions for both dough processes are shown in Table 1.[1/]

In the straight dough process, the ingredients are mixed until a smooth dough is obtained. After the dough ferments for 2 to 4 hr at 78 to 82°F, it is kneaded and allowed to ferment for 20 to 30 min. Next, the dough is divided, panned, and allowed to ferment at 95 to 105°F for up to 60 min. Finally, the dough is baked at 460°F. The bread is allowed to cool before packaging.

TABLE 1. STRAIGHT DOUGH AND SPONGE-DOUGH FORMULATIONS

	Straight	Sponge-dough	
		Sponge	Dough
Flour[a/]	100.0	65.0	35.0
Water (variable)	65.00	40.0	25.0
Yeast	3.0	2.5	-
Yeast food	0.2-0.5	0.2-0.5	-
Salt	2.25	-	2.25
Sweetener (solid)	8-10	-	8-10
Fat	3.0	-	3.0
Nonfat milk solids	3.0	-	3.0
Softener	0.2-0.5	-	0.2-0.5
Rope and mold inhibitor	0.125	-	0.125
Dough improver	0-0.5	-	0-0.5
Enrichment	as needed	-	as needed

a/ Ingredients based on 100 parts flour.

In the sponge-dough process, a portion of the flour and water are mixed with yeast and yeast food. This sponge ferments for 3.5 to 5 hr at 80°F. The rest of the ingredients are then added and mixed, and the dough is fermented for another 20 to 30 min. Then the dough is divided, rounded and panned, and allowed to ferment for 60 min. Finally, the dough is baked at approximately 460°F for up to 20 min. The bread is cooled before packaging. A detailed description of these processes is presented in Reference 1.

SECTION 3

EXPERIMENTAL APPARATUS AND PROCEDURE

In order to measure the emissions of organics during each stage of the breadmaking process, the dough was enclosed in a plastic tent. Air was withdrawn continuously from the top of the tent by the sampling instrument, a gas chromatograph. Air entered at the bottom of the tent to replace the air withdrawn at the top. A schematic of the laboratory apparatus is shown in Figure 1.

The dough was baked in an electric oven which had three exhaust ports on its top side (see Figure 1). Proper operation of the oven shown in Figure 1 required the ports in the top to be left open. The flow rate of the air from these ports was measured to determine the quantity of air moving through the oven, and thus the dilution of the emissions by the air flowing through the oven. Samples for organics analysis were taken from the exhaust stream just inside the oven.

The concentrations of organics in the sampling stream were determined with a Beckman Model 6800 Air Quality Chromatograph (total hydrocarbon analyzer) operating under its normal conditions (no special adaptations). A stainless steel bellows pump inside the chromatograph pulled the sampling stream from the tent or oven into the chromatograph at a continuous rate of 800 cu cm/min. At 5-min intervals, the chromatograph measured the organic concentration in the sampling stream. The chromatograph was calibrated with gas containing 5.1 ppm total hydrocarbons consisting of methane.

Because of the high organic concentrations found in the experiment involving the straight dough process (August 4, 1977), a dilution system was constructed to reduce concentrations in the subsequent experiment involving the sponge-dough process (November 15, 1977). The dilution system, which was used to reduce the concentration of organics by as much as a factor of 100, involved the use of two gas flow meters to determine the flow rates of the dilution air and the undiluted sampling stream. The chromatograph sampled from the diluted stream.

The ambient air was sampled periodically to determine the background organics concentration in the air entering the tent and oven. Since the air was drawn into the tent and oven to replace the air removed by the sampling stream, no losses of emitted organics were expected from the bottom of the tent or oven.

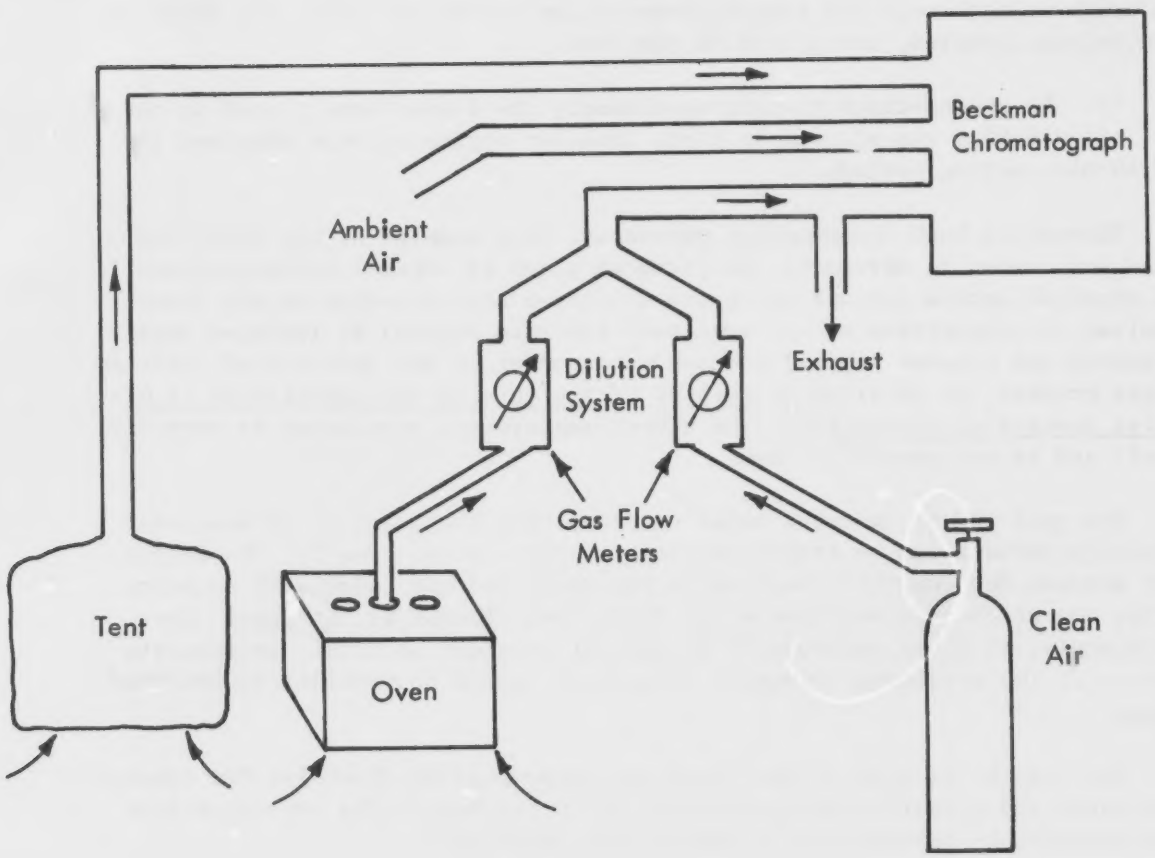


Figure 1. Experimental Apparatus

The sampling stream exhaust port shown in Figure 1 was directed into an exhaust hood which removed the air from the room.

The experiments began with the measuring of the weights of each ingredient. The ingredients were mixed and the dough was placed inside the tent for the appropriate time. The chromatograph pump pulled air from the tent continuously.

Next, the dough was kneaded (inside the tent) in the straight dough process, or mixed with the rest of the ingredients in the sponge-dough process. The dough went through its second fermentation inside the tent. The dough was then panned, proofed, and placed in the oven.

For the sponge-dough process experiment, the loaves were placed in the tent after baking and allowed to cool. Emission estimates were obtained for the 40-min cooling period.

Throughout both breadmaking processes, 20-g samples of the dough and bread were taken to determine the inverted sugar or ethanol concentrations. The chemical method for determing the sweetener concentration in the dough involved the conversion of the sweetener (sucrose sugars) to inverted sugars (fructose and glucose sugars) and the measurement of the quantity of inverted sugars present, as detailed in Methods of Analysis of the Association of Official Analytical Chemists.[2/] The direct measurement of sucrose is very difficult and is not generally used.

The quantity of inverted sugar expected from the quantity of sweetener initially present can be stoichiometrically calculated. Ideally, the difference between the quantity measured in the dough and the calculated quantity is the amount of sweetener converted to CO_2 and ethanol by the yeast. Unfortunately, in these experiments it was not possible to obtain an accurate measure of the sweetener converted because of starch conversions to inverted sugar.

The ethanol present in the bread was determined by absorbing the ethanol into water and measuring the concentration in the water. The concentrations were measured by standard gas chromatograph techniques.

Both the sweetener and ethanol concentrations were related to the quantity of dough or bread in the sample to give a concentration in the dough or bread at the time the sample was taken.

SECTION 4

EXPERIMENTAL DATA

STRAIGHT DOUGH PROCESS

On August 4, 1977, an experiment was conducted to determine the emission rates of nonmethane organics from bread dough mixed by the straight dough process. The weight of the mixed dough was 1,480 g (3.3 lb) with a sugar concentration of 3% (45 g (0.1 lb)). A listing of the ingredient weights is given in Table 2. The yeast and other ingredients were obtained from a local grocery store. The yeast was not of a type acclimated specifically to bread dough.

TABLE 2. INGREDIENTS AND PROCEDURE FOR STRAIGHT DOUGH PROCESS

*	Ingredients: 895 g flour, 360 g water, 102.5 g milk, 57 g margarine, 45 g sweetener, 14 g salt, 11 g yeast
*	Mix well (10 min)
*	Let rise (3 hr)
*	Knead (15 min)
*	Let rise (1 hr)
*	Pan (10 min)
*	Bake (40 min)

After mixing, a 20-g sample was taken for analysis to determine the sugar concentration in the dough. The analysis indicated a concentration of 5.3%, by weight, of sugar in the dough, which is higher than would be expected from the quantity of sweetener added to the dough. This may be due to conversion of some of the flour to inverted sugar by the yeast. The error in the quantitative analysis was less than 5%.

The dough was placed in the tent for its first 3-hr fermenting period. Then the dough was kneaded for 15 min inside the tent and allowed to rise for another 60 min. Finally, the dough was formed into two loaves, approximately equal in weight, and then baked for 40 min at 360°F.

Throughout the experiment, two chromatographs were used to follow the organics emitted from the dough. The Beckman chromatograph measured the total nonmethane organic concentration in the sampling stream. The other chromatograph, a Varian 2400 Gas Chromatograph, simultaneously measured the ethanol concentration in the sampling stream. The Varian chromatograph used a Chromosorb 102 column at 120°C and an FID detector. Examples of the output of the Beckman and Varian chromatographs are shown in Appendix B.

After the bread was removed from the oven, it was weighed. Also, samples were taken for analysis to determine the inverted sugar content and ethanol concentration in the bread. The inverted sugar concentration was 4.9%, and the ethanol concentration in the bread was less than 0.2%. A summary of the times, weights, and the inverted sugar and ethanol concentrations are shown in Table 3. The data from the experiment is included in Appendix C.

The chromatographs measured concentrations of organics in parts per million by volume in the sampling stream. These concentrations were converted to mass emission rates by using the sampling stream flow rate, molar weight of ethanol and the molar volume of ethanol. The concentration of the sampling stream was adjusted by the dilution ratio. An example of the calculations is shown in Appendix B.

The ethanol emission rates measured during the experiment are shown plotted in Figure 2. Graphical integration of this curve results in the total emissions of ethanol during the time period. The value obtained when integration was carried out using 10-min interval values was 0.71 g.

When the concentration of ethanol was compared with the concentration of total nonmethane organics, it was found that 95% of the nonmethane organics emitted by the dough was ethanol. Three organic compounds constituted the other 5% of the nonmethane organics emitted. These three organics were of low molecular weight and may have been aldehydes or alcohols.

The total ethanol emissions of 0.71 g from 1,282 g bread when converted to the emissions per kilogram of bread produced the following emission factor for the straight dough process:

Ethanol emissions: 0.5 g ethanol/kg bread produced
(0.5 lb/1,000 lb bread)

The emissions during baking made up 77% of the total emissions measured, while the other steps accounted for 23% of the emissions.

The emissions measured were approximately 6% of the factor predicted by Mr. Henderson in his paper. The discrepancy between the values may be due to the initial sugar concentration and the type of yeast used. It is

TABLE 3. STATISTICS FOR THE BREADMAKING EXPERIMENT - STRAIGHT DOUGH PROCESS

	Mixed	End of first rise	End of kneading	End of second rise	End of baking
Time elapsed (min)	0	210	240	320	370
Dough weights (g)	1,480	a/	1,377	1,373	1,282
Inverted sugar concentration	5.3% (dough)	a/	a/	a/	4.9% (bread) b/
Cumulative Emissions (g ethanol)	0	0.04	0.05	0.09	0.71

a/ Not measured.
b/ By weight, as determined by chemical analysis. This includes sucrose added as sweetener as well as any natural sugars present.

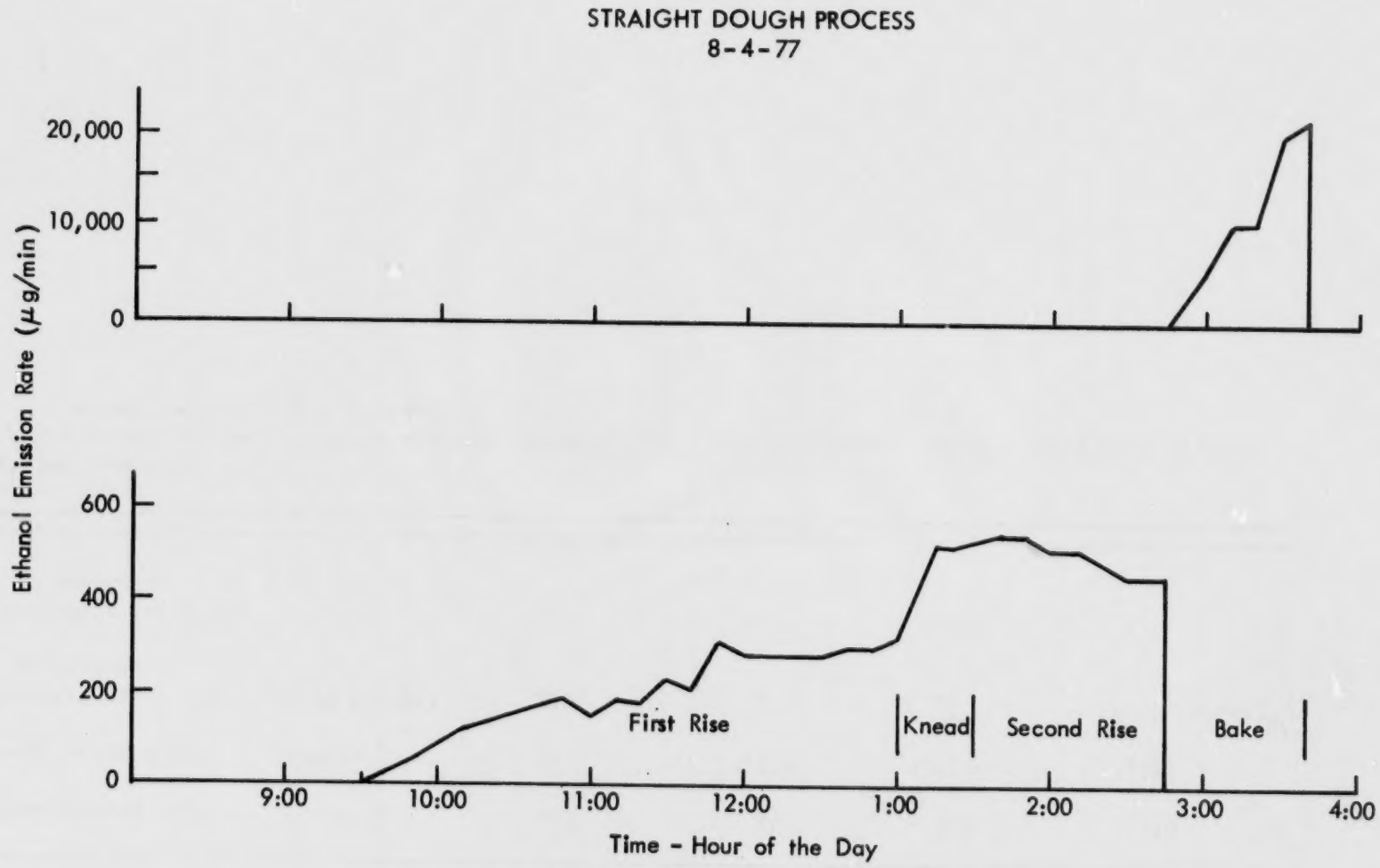


Figure 2. Ethanol Emission Rate

reasonable to assume that a larger concentration of sugar in the dough would result in greater production of ethanol and CO_2. The yeast used was an off-the-shelf variety rather than a special yeast acclimated to the conditions of commercial bread producing. It would be expected that the emission factor would increase with increased sugar content and the use of the proper yeast. However, the degree of increase cannot be accurately predicted without knowing the specific relationship of emission rate to sugar content and yeast type.

Initially, it was believed that a mass balance could be constructed using the quantity of (a) sugar consumed (inverted sugar concentrations); (b) ethanol emitted; and (c) the quantity of ethanol in the bread after baking. However, this was not the case since it is possible for the yeast to break down the flour to form inverted sugars and thus ethanol. The concentrations of inverted sugars and ethanol have been included in this report for the reader's reference.

SPONGE-DOUGH PROCESS

On November 15, an experiment was conducted to measure the emission of ethanol during bread production using the sponge-dough process. The experiment was designed to measure ethanol emissions with the Beckman total hydrocarbon analyzer during rising, proofing, baking, and cooling. It was assumed that ethanol was the major organic component of the emissions.

Because of the high emissions expected, a dilution system was devised that could dilute the emission by a factor of 100 to 1. Two gas flow meters were used to measure the flow rates of the emissions sampling stream and dilution air. The chromatograph sampled from this diluted stream to measure the ethanol concentration.

The dough was mixed according to the directions of Reference 1. The procedure and ingredients were as shown in Table 4. In the total dough mix (after samples) of 1,126.5 g, the sugar concentration was 6.2%.

Samples were taken throughout the process for determination of the inverted sugar concentration. Samples were taken after the initial mixing, at the end of the first rise, after the final mixing, before baking, and after baking. These concentrations are shown in Table 5 along with the time schedule and dough weights. The dough was divided into 2 loaves when it was panned. The total dough weights are shown.

The ethanol concentration in the bread after it was taken from the oven was found to be 1 ppm by weight. The low value indicates that very little ethanol remains in the bread.

The experiment measured the emissions of ethanol during the first rise period, second rise period, while baking, and as the bread was cooling. The emission rates for the experiment are shown in Figure 3. These were obtained

TABLE 4. INGREDIENTS AND PROCEDURES FOR THE SPONGE-DOUGH PROCESS

*	Ingredients: 490 g flour, 455 g water, 21 g acclimated yeast, 3.5 g yeast food
*	Combine ingredients, mix well
*	Allow to rise for 3.5-4.5 hr
*	Add: 210 g flour, 70 g sweetener, 21 g fat, 21 g milk, 16 g salt
*	Mix
*	Allow to rise for 20-30 min
*	Divide and pan
*	Let rise for 60 min
*	Bake
*	Cool

in a similar manner as described for the August 4 experiment. The experimental data are included in Appendix C. Graphical integration of these rates yields a factor of 4.6 g of ethanol per kilogram of bread produced. The emissions during baking constitute 99% of the total emissions. These emissions of 4.6 g/kg of bread are approximately half of those estimated by Mr. Henderson.

The inverted sugar concentrations and ethanol concentrations were not useful in a mass balance because of the conversion of flour to inverted sugars. They are presented for the reader's reference.

TABLE 5. STATISTICS FOR THE BREADMAKING EXPERIMENT - SPONGE-DOUGH PROCESS

	Mixed	Total mix	Before baking	After baking
Time elapsed (min)	0	240	330	515
Dough weights (g)	969.5	1,175	1,126.5	947.8
Inverted sugar concentrations	1.2%	5.3%	6.7%	5.4%
Cumulative emissions (g of ethanol)	0	0.003	0.004	4.4

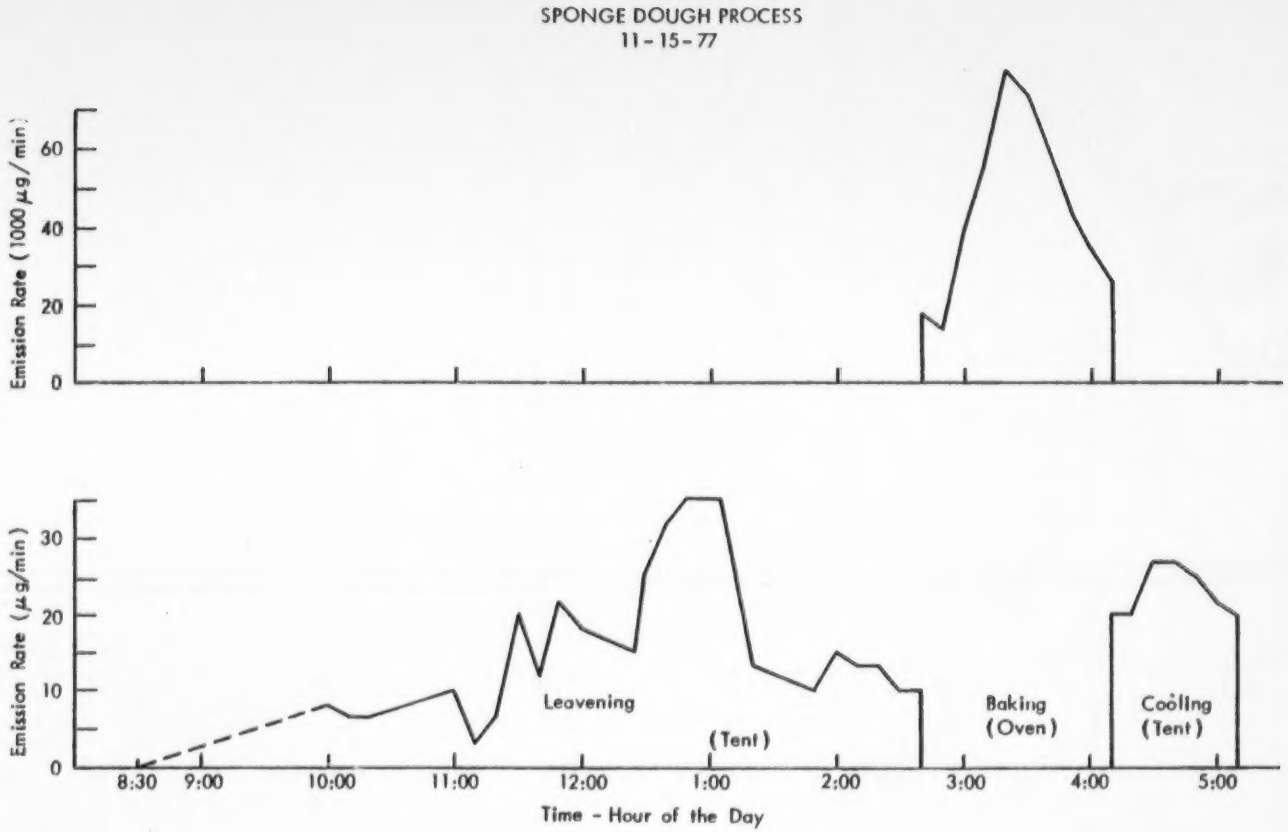


Figure 3. Ethanol Emission Rate

SECTION 5

DISCUSSION

In attempting to apply the experimental data presented in this report to commercial bakeries, at least three factors affect the application. First, the production processes in bakeries use machines to mix, knead, and pan, as well as for most of the other operations. Furthermore, the processes take place in temperature and humidity controlled rooms. The machines and environmental conditions will have some effect on the production of ethanol in the nonbaking steps of the processes.

Secondly, the sweetener content is generally 8 to 10% of the dough weight. This work has assumed a linear relationship between emissions and sweetener concentration to compare expected and experimental emissions. This relationship has not been tested and may introduce error.

Finally, another factor not considered in this work is the effect of the natural gas burners on the emissions. If the ethanol emissions reach the flames or are heated to a sufficient temperature, they will be burned. This will result in lower stack emissions from bread baking than predicted by this work.

In discussing this possibility with one baking expert,[3/] it was found that most bread baking is done in ovens which fire at the bottom with hot air passing up and around the dough with the temperature of the dough not exceeding 500°F. There is a possibility that in certain regions of the oven, flames may reach the ethanol vapors, but this is not likely.

For cakes and some pastry items, the oven has flames above and below the dough. In these ovens, the possibility of flames reaching the ethanol vapor is very high. Therefore, in these types of ovens, ethanol emissions would be expected to be reduced.

The effect of the above variables on emissions can best be determined by field tests at a commercial bakery.

SECTION 6

RECOMMENDATIONS

The experimental work reported here indicates that nonmethane organic emissions occur during the production of bread. These emissions were found to consist primarily of ethanol, mostly generated during baking. A more representative estimate of the emissions from bread production would be obtained if the sponge-dough process experiment would be repeated using 10% sweetener concentration.

The next step in determining the organic emissions from bakeries would be field experimentation at a bakery site. Since the majority of the emissions occur during baking, stack sampling of the oven exhaust would have highest priority. The emissions measured on-site would be representative of the true bakery conditions.

REFERENCES

1. Pomeranz, Y. Editor. Wheat/Chemistry and Technology. Published by the American Association of Cereal Chemists, St. Paul, Minnesota, 1971. p. 676.

2. Harwitz, W. Editor. Official Methods of Analysis of the Association of Official Analytical Chemists. Published by the Association of Official Analytical Chemists, Washington, D.C., 1975.

3. Personal communication with representative of Interstate Brands, Kansas City, Missouri, July 1975.

APPENDIX A

COMMERCIAL BAKERIES AS A MAJOR SOURCE OF REACTIVE VOLATILE ORGANIC GASES

ENVIRONMENTAL PROTECTION AGENCY

REGION IX

SURVEILLANCE & ANALYSIS DIVISION

Title: Commercial Bakeries as a Major Source of Reactive Volatile Organic Gases

Prepared By: David C. Henderson
Environmental Engineer
Air Section, Air & Hazardous Materials Branch
Surveillance & Analysis Division, EPA Region IX
215 Fremont Street
San Francisco CA 94105
(415) 556-8047

Date: December, 1977

Summary:

The baking industry appears to represent a major source of photochemically reactive volatile organic gases in the form of ethyl alcohol and other gases. Yeast fermentation of bread baking doughs produces pyruvic acid and acetaldehyde as intermediate products and about equal molar amounts of ethyl alcohol and carbon dioxide gas (CO_2) as final products. Recent source tests performed by an EPA contractor have validated theoretical estimates of the magnitude of the emissions. Emission factors are presented in this paper on a per capita and production rate basis. Large bakeries can emit up to 168 tons/year of ethyl alcohol.

Purpose:

The purpose of this report is to provide information on volatile organic gas emissions from the baking industry in order that emission estimates can be included in emission inventories currently being developed in EPA, Region IX.

Background:

The art of bread baking has changed little in the 2,000 years since the Egyptians discoverd the leavening of bread. The basic ingredients of bread are flour, water, salt, sugar, and yeast. Other ingredients are added to enhance the flavor or texture of the desired product.

The role of the yeast in bread baking is to produce carbon dioxide gas. The evolving CO_2 raises or "leavens" the bread dough to a desired volume. Yeast produces the CO_2 by anaerobically decomposing the sugar in the natural metabolic process known as alcoholic fermentation. Alcoholic fermentation of sugar by yeast produces equal amounts of CO_2 gas and ethyl alcohol, with pyruvic acid and acetaldehyde also produced as intermediaries.

In a commercial bakery, bread dough is allowed to ferment from two to four hours prior to baking at an oven temperature of 450°F. The temperature inside the bread does not exceed 212°F. The ovens used in commercial bread bakeries are predominately fired by natural gas and are direct fired. In direct fired ovens, any vapors driven off the bread and any combustion product gases are removed throught the same exhaust vent. The aroma associated with fresh baked bread, in the locale of a bakery, is actually fermentation of alcohols, aldehydes, and possibly other organics being emitted to the atmosphere.

It is believed that alcohol is produced as a liquid within the bread dough during the fermentation period.[1] Part of the alcohol is driven off the bread during oven baking. Since the oven is operating at 450°F, it may be possible that the alcohol is undergoing a chemical reaction, such as dehydrogenation to form aldehydes or esters, before it is exhausted from the oven.

Also since a carboxylic acid (pyruvic) and acetaldehyde are produced as intermediaries, these substances too could be undergoing some type of chemical reaction prior to being exhausted from the oven.

Bakery products can be divided into two groups; products that are yeast leavened, and products which are chemically leavened by baking powder. This review is only concerned with yeast leavened bakery products. Yeast leavened bakery products include most breads, sweet rolls, sweet yeast goods, ordinary crackers, pretzels, and doughnuts excepting cake doughnuts. Chemically leavened bakery products include cakes, cookies, cake doughnuts, and quick breads such as corn bread or baking powder bisquits.(2)

STOICHIOMETRY AND MECHANISM OF ALCOHOLIC FERMENTATION BY YEAST:

The following chemical reactions occur during yeast fermentation of sucrose:

$$\underset{\text{(sucrose)}}{C_{12}H_{12}O_{11}} + HOH \longrightarrow \underset{\text{(fructose)+(glucose)}}{C_6H_{12}O_6 + C_6H_{12}O_6}$$

$$2C_6H_{12}O_6 \xrightarrow[\text{enzymes}]{\text{yeast}} \underset{\text{(pyruvic acid)}}{4CH_3COCOOH}$$

$$4CH_3COCOOH \xrightarrow[\text{enzymes}]{\text{yeast}} \underset{\text{(acetaldehyde)}}{4CH_3CHO} + 4CO_2$$

$$4CH_3CHO \xrightarrow[\text{enzymes}]{\text{yeast}} 4CH_3CH_2OH$$

(ethyl alcohol)

CALCULATION OF ETHYL ALCOHOL PRODUCED PER TON OF SUCROSE CONSUMED:

For each mole of sucrose consumed four moles of ethyl alcohol are produced.

Molecular weight of sucrose =

$$_{12} = 12 \times 12 = 144$$

$$H_{22} = 22 \times 1 = 22$$

$$O_{11} = 16 \times 11 = 176$$

342 lb./lb. mole

The number of pound moles of sucrose in 1 ton =

$$\frac{\text{lb. moles}}{\text{ton sucrose}} = \frac{\frac{2000 \text{ lb.}}{\text{ton}} \quad \frac{1 \text{ lb. mole}}{342 \text{ lb.}}}{} = 5.8$$

Since for each mole of sucrose consumed four moles of alcohol are produced, therefore, for each ton of sucrose consumed there are 23.4 lb. moles of alcohol produced.

$$\frac{5.8 \text{ lb. moles sucrose}}{} \quad \frac{4 \text{ lb. moles alcohol}}{} = \frac{23.4 \text{ lb. moles alcohol}}{\text{ton sucrose}}$$

Molecular weight of ethyl alcohol =

$$C_2 = 12 \times 2 = 24$$

$$H_6 = 6 \times 1 = 6$$

$$O = 16 \times 1 = 16$$

46 lb./lb. mole

Pounds of ethyl alcohol produced per ton of sucrose consumed is =

$$\frac{\text{lb. ethyl alcohol}}{\text{ton sucrose}} = \frac{23.4 \text{ lb. moles alcohol}}{\text{ton sucrose}} \quad \frac{46 \text{ lb.}}{\text{lb. mole alcohol}}$$

$$= \frac{1076 \text{ lb. ethyl alcohol produced}}{\text{ton sucrose consumed}}$$

$$\text{or,} \quad = \frac{.54 \text{ lb. ethyl alcohol produced}}{\text{lb. sucrose consumed}}$$

However, it is not necessary for sucrose or any other sweetener to be added to the bread for alcohol to be evolved. In the absence of a carbohydrate sweetener, the yeast will reduce carbohydrates in the wheat to maltose and ultimately to ethyl alcohol and carbon dioxide. A good example of a bread made without an added sugar is some of the San Francisco sour dough breads.

Therefore, the amount of ethyl alcohol could be greater than the value calculated for each pound of sucrose consumed.

ESTIMATION OF BAKERY EMISSIONS BASED ON BREAD PRODUCTION RATES:

The nation's largest bread baker, Continental ITT[3] and the major manufacturer of commercial baking ovens, Baker-Perkin[5] were contacted to determine if any studies had been conducted or tests performed to establish volatile organic gas emissions from the fermentation process in commercial bakeries. It was learned that there is no reliable information available to estimate emissions from the baking industry. A source test was performed

by Baker-Perkin's contractor, Clayton Environmental, during August, 1974, on a direct fired commercial bakery oven. The hydrocarbon emission rate from this test was determined to be 1 lb. HC/1000 lb. bread. However, according to Continental ITT, this test only measured hydrocarbons (i.e. compounds containing only hydrogen and carbon). Ethyl alcohol, acetaldehyde, and pyruvic acid are not strictly hydrocarbons as they contain oxygen in addition to hydrogen and carbon. Also, the test was considered to be unreliable and not reproducible by Continental ITT observers on the scene.

Continental ITT is the largest baker in the country, producing Wonder Bread, Hostess Cupcakes, Hostess Twinkies, and many other name brand baked goods. At the request of the EPA Regional Office, Continental ITT's Research Department developed an estimated emission factor of:

$$\frac{\text{8.0 lb. ethyl alchohol emitted}}{\text{1000 lb. bread baked}}$$

The emission factor estimated by Continental ITT is based on the following assumptions:

(1). 8-10% of bread's dough weight is sugar

(2). 10-15% of sweet rolls' dough weight is sugar

(3). Only 2-3% of the bread or seeet rolls' dough weight is consumed and attributable to alcoholic fermentation

(4). 50% of the dough weight loss is converted to alcohol

(Note - this correlates well with the weight of alcohol produced per pound of sugar consumed, which was calculated as 54% earlier in this report.)

(5). Some of the alcohol remains in the bread

(Note - Continental ITT is estimating that between 25% and 53% of the alcohol produced remains in the bread.)

Based on the information provided by ITT Continental, it was calculated that a large commercial bakery could emit over 100 tons/year of volatile organic gases.

In order to develop an accurate estimate of emissions from this source, EPA contracted with Midwest Research Institute (MRI), Kansas City, Missouri, to perform source tests.[7] The first test was conducted during August, 1977. Two loaves of bread, each weighing approximately 1.6 pounds were baked in the laboratory. A straight dough mix was used with a sugar concentration of 5.3% by dough weight. Plastic tents were constructed over the areas where the bread was mixed, kneaded, and allowed to rise. Sampling probes were placed in the oven during baking.

A gas chromatograph (G.C.) sampling pump continuously withdrew samples for analysis from within the plastic tent. The emission rates of the hydrocarbons were obtained by knowing the

flow rate of the G.C. sampling pump and obtaining the concentration on the flow stream from the G.C. An overall emission factor of about .8 lb. ethyl alcohol per pound of bread produced was calculated from this test data. However, this test was not considered valid for the following reasons:

1. The bread mix was straight dough and not a commercial sponge dough process. Home baked breads are normally straight dough mixes while commercial breads are normally sponge dough mixes.
2. The sugar concentration in the straight dough mix was only 5.3%. Sponge dough mixes would contain approximately 10% sugar.
3. The testing was discontinued when the bread was removed from the oven which is at the peak of its ethyl alcohol emissions.
4. The yeast used was not a commercial grade yeast.

A second laboratory test was conducted in November, 1977, by MRI. In this test, a sponge dough mix was used and the yeast was a commercial grade obtained from the local Wonderbread bakery. However, the sweetener concentration in the dough was only 5%.

In this test, the cumulative emission factor for the entire baking process was approximately 3.0 lb. of ethyl alcohol emis-

sions per 1000 pounds of bread produced. Almost the entire amount of this emission is evolved during the baking phase.

Based on these two tests, there appears to be a linear relationship between sweetner concentration and emissions. If this assumption is correct, then ethyl alcohol emissions of approximately 8.0 lb./1000 lb. of bread would be expected from a commercial dough mix with a sweetener concentration of 10%.

During January, 1978, it is expected that M.R.I. will complete a third experiment, using a sweetner concentration of 10%. A final report, including all test data, should be available from M.R.I. after this test is completed.

CALCULATION OF EMISSIONS FOR A LARGE COMMERCIAL BAKERY

Using this emission factor, a calculation was made for a large commercial bakery.

Assuming that a large commercial bakery:

(1) produces 12,000 lb. bread/hr.;

(2) operates 14 hr./day;

(3) operates 250 day/year,

the calculated emissions for this bakery using the Continental ITT emission factor would be:

$$\text{alcohol} = \frac{1 \text{ ton}}{2000 \text{ lb.}} \quad \frac{12{,}000 \text{ lb. bread}}{\text{hour}} \quad \frac{8.0 \text{ lb. alcohol}}{1000 \text{ lb. bread}} \quad \frac{14 \text{ hr.}}{\text{day}} \quad \frac{250 \text{ days}}{\text{year}}$$

$$\frac{\text{ethyl alcohol emitted}}{\text{year}} = \frac{168 \text{ tons}}{\text{year}}$$

This estimate represents the worst case situation, as it is an example of a very large commerical bakery. A small commercial bread bakery may produce only 2,000 lb./hr and only operate 8 hours per day.

ESTIMATION OF BAKERY EMISSIONS ON A PER CAPITA BASIS:

The following table lists annual yeast leavened baked goods production, excluding retail single-shop bakeries:

PRODUCTS	THOUSAND POUNDS/YEAR
White bread	8,861,343
White hearth bread	426,998
Whole wheat and other dark wheat breads	643,216
Rye breads	509,545
Raisin and other speciality breads	419,506
Rolls-bread type	2,063,124
Sweet yeast goods	875,053
Crackers	1,369,194
Pretzels	139,380
Total	15,307,359

The source of this information is the U.S. Census Bureau for the year 1966. However, it is reported that these figures have not changed appreciably in recent years.(2) Although single retail bake shops are not included in this listing, they are not considered to be a major factor in the baking industry.

The population of the United States for 1976 was 213.6 million.[6]

$$\frac{\text{lb. yeast leavened bake goods consumed}}{\text{person-year}} =$$

$$\frac{15,307,359,000 \text{ lb. bake goods}}{213,600,000 \text{ person-year}}$$

$$= 71.7 \text{ lb.} \frac{\text{yeast leavened bake goods consumed}}{\text{person-year}}$$

Using the emission factor of 8.0 lb. ethyl alcohol emitted/ 1000 lb. baked goods, the ethyl alcohol per person per year would be:

$$= \frac{8.0 \text{ lb. ethyl alcohol emitted}}{1000 \text{ lb. bake goods}} \quad \frac{71.7 \text{ lb. bake goods}}{\text{person-year}}$$

$$= \frac{.57 \text{ lb. ethyl alcohol emitted}}{\text{person-year}}$$

It should be noted that this estimate includes emissions from cracker and pretzel baking which comprise less than 10% of the total production of yeast leavened bake goods. The emission factor of 8.0 lb. alcohol emitted per 1000 lb. bread baked, estimated by Continental ITT, does not apply to crackers and pretzels, as these products are not manufactured by this company. However, lacking any additional information, the Continental ITT emission factor was also applied to cracker and pretzel baking.

ESTIMATE OF BAKERY EMISSIONS IN THE SOUTH COAST AIR BASIN:

For illustrative purposes, an estimate of bakery emissions for the approximately 11 million people residing in California's South Coast Air Basin (greater metropolitan Los Angeles area) would be:

$$= \frac{.57 \text{ lb. alcohol emitted}}{\text{person-year}} \quad \frac{11{,}000{,}000 \text{ persons}}{}$$

$$= \frac{6{,}270{,}000 \text{ lb. ethyl alcohol emitted}}{\text{year}}$$

Or, $$= \frac{6{,}270{,}000 \text{ lb.}}{\text{year}} \quad \frac{1 \text{ ton}}{2{,}000 \text{ lb.}}$$

$$= \frac{3{,}135 \text{ tons}}{\text{year}} \quad \frac{1 \text{ year}}{365 \text{ days}}$$

$$= \frac{8.6 \text{ tons}}{\text{day}}$$

The total stationary source emissions on non-methane organics in the South Coast Air Basin for 1974 are estimated at 651 ton/day.[7] The percentage of emissions from stationary sources in the South Coast Air Basin due to bakeries is:

$$= \frac{\frac{8.6 \text{ ton}}{\text{day}} \quad 100}{\frac{651 \text{ ton}}{\text{day}}}$$

$$= 1.3\%$$

The following table compares emissions from commercial bakeries in the South Coast Air Basin to other major source categories; for Non-Methane Hydrocarbons (NMHC) for 1974:[6]

Stationary Source Category	% Total NMHC Emissions
Miscellaneous Organic Solvent Usage	26.8
Surface Coating (Painting, etc.)	25.5
Petroleum Marketing	24.0
Petroleum Refining	7.3
Solvent Degreasing	5.8
Dry Cleaning	4.4
Structural Fires	4.2
Utility Equipment (lawn mowers, etc.)	3.1
Wild Fires	2.3
Pesticides	1.4
Commercial Bakeries	1.3
Power Generating Plants	1.3
Petroleum Refining-Fuel Combustion	.8
Orchard Heaters	.6
Industrial Fuel Combustion	.5
Petroleum Production	.4
Metallurgical Processing	.4

According to this estimate, commercial bakeries would be the 11th largest NMHC emission category, within the South Coast Air Basin, according to this system of classifying sources.

BIBLIOGRAPHY

(1) Private commmunication, Mr. Robert Mantsch, Red Star Yeast Company, Universal Foods Corporation, Milwaukee, WI (414) 271-6755, May, 1977.

(2) McGraw-Hill Encyclopedia of Science and Technology, 1971, Volume 5, page 445.

(3) Private communication, Mr. Peter Tobiason, ITT Continental Baking Co., Inc., Rye, New York, (914) 967-4747, May, 1977.

(4) Private communication, Mr. Petri, Baker-Perkin Corp., Saginaw, Michigan, (517) 752-4121, May, 1977.

(5) Statistical Abstracts of the U.S., 1976, U.S. Bureau of the Census.

(6) Preliminary Emissions Inventory and Air Quality Forecast 1974-1994, Final Report, Air Quality Maintenance Planning Task Force, South Coast-Southeast Desert Air Quality Maintenance Areas, Final Report, May, 1976.

(7) Preliminary Test Results, conducted on August 4, 1977 and November 15, 1977, Midwest Research Institute, Kansas City, Missouri. Mr. Ralph Keller, Project Officer, (816)753-7600.

CONDENSED DISCUSSION

Question: What type was the oven and how did you sample the emissions from it?

Keller (MRI): Our oven was an electric heating oven. We had three holes in the top of the oven and we had glassware coming out of the holes and hooked into our GC. We had flow rate measured out the top. We thus knew the concentration and the flow rate coming out the top. We also believe because of our realitively high flow rate coming out of the oven, we did not have any organics turning back onto the electric heaters on the bottom of the oven.

Question: How did you measure flow from the first of the operation?

Keller: The GC unit has a sampling rate of 2.8 cubic feet per minute. The holes were stuck into a bag that had an inlet that was just open to clean air so that the GC pulled out 2.8 and supposedly clean air came in at 2.8.

Question: How do you feel about the statistical significance of only using two loaves for developing emissions factor? You only did two loaves - you are going to do two more.

Keller: Yes, 1500 grams.

Question: Why not make 20 or 30 continuously so you identify the different variances?

Henderson: Well we are not baking 20 or 30 because of money constraints. It took six man days to do the analysis and baking of just two loaves of bread. This is quite a lot of money. I believe that the two or four loaves we make will provide fairly representative emission factors. We will be using a process similar to what bakers use and we are making sure our bread and dough is homogenious and that it is representative of the "standard" loaf of bread.

Keller: Again, this was a first look to see how close we came to the theorical values. If we come out the second time and we find we are far off then we may discuss with the project officer to see if we should load up our equipment, contact a baker and go out to get field samples.

Question: What were the other species that you measured besides ethyl alcohol? Was there anything else picked up in the GC?

Keller: We found the ethyl alcohol was 95% of the hydrocarbons coming out. There was no methane. The other 5% of hydrocarbons had a boiling point similar to ethanol. As we pointed out there are a couple other organic species that could be coming out, but we did not sample to see what they were. We also did not sample the water emission rate.

APPENDIX B

SAMPLE CALCULATIONS

The calculation of the emission rate for organics involves the adjustment of the concentration reading from the chromatographs for the dilution of the emissions and the conversion of the concentration by volume to an emission value expressed in terms of mass/time. Examples of the output of the two chromatographs are shown in Figure B-1 (Varian) and Figure B-2 (Beckman).

A concentration is obtained from these graphs by subtracting the portion of the peak height due to background organic concentrations and multiplying by the calibration value (ppm/cm of peak height).

This concentration is then multiplied by the ratio of the total sampling stream flow rate to the sampling stream flow rate out of the tent or oven. The molecular weight of methane and the molar volume at room temperature are then used to produce a mass emissions value.

Next, the response of the chromatograph to ethanol is taken into account. A value of 0.28 was determined for this chromatograph by injecting known quantities of ethanol.

An example of this procedure follows.

Example: Sponge-Dough Process, November 15, 1977, 3:30 PM, During Baking

- Calculation of organics concentration (ppm) from Beckman chromatograph data:

  Peak height: 32 cm
  Background: 24 cm
  Calibration: 0.137 ppm/cm

  Oven dilution factor: 1050 = total oven air flow rate ÷ sampling rate of chromatograph.

  Concentration = (32-24) x 0.137 x 1050 = 1150 ppm as methane.

- Conversion of ppm to μg/min:

  C = concentration expressed as methane (ppm by volume)
  V = flow rate (cc/min)
  16 g = methane molecular weight
  24.5 liters = molar volume; 25°C, 1 atm
  0.28 = response factor of chromatograph to ethanol

- Emission rate $= C \frac{\ell}{10^6 \ell} \cdot V \frac{cc}{min} \cdot \frac{16\ g}{mole} \cdot \frac{1\ mole}{24.5\ \ell} \cdot \frac{\ell}{10^3\ cc} \cdot \frac{10^6\ \mu g}{g} \cdot \frac{1}{0.28}$

$$= C \cdot V \cdot 1.4 \times 10^{-3} \frac{\mu g}{min}$$

$$= 1150 \cdot 2.74 \times 10^4 \cdot 2.3 \times 10^{-3} = 73500\ \mu g/min$$

Note: $V = 2.74 \times 10^4$ cc/min obtained from raw data table in Appendix C for sponge-dough process.

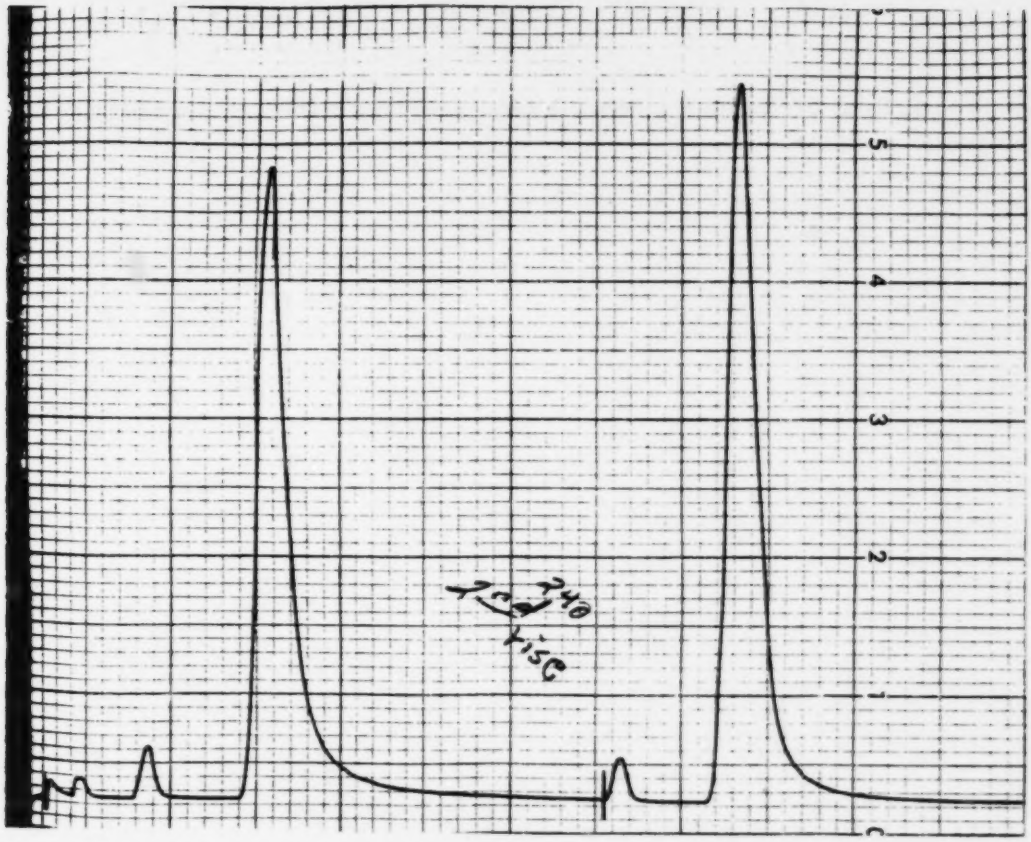


Figure B-1. Varian Chromatograph Output

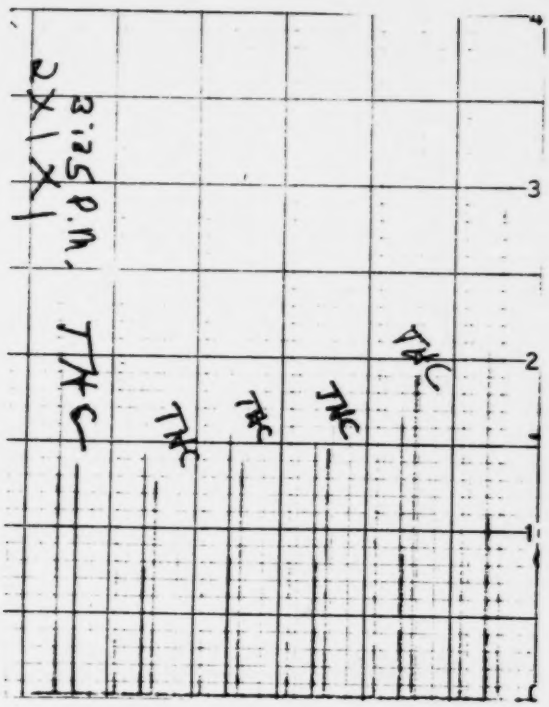


Figure B-2. Beckman Total Hydrocarbon Analyzer Output

APPENDIX C

RAW DATA FOR THE TWO EXPERIMENTS

AUGUST 4, 1977 BREADMAKING EXPERIMENT
STRAIGHT DOUGH PROCESS

Time	Time elapsed (min)	Nonmethane organics: Concentration expressed as methane (ppm)	Nonmethane organics: Ethanol emission rate (μg/min)	Accumulated ethanol emissions (μg)	Comments
9:30 AM	0	0	0		First rise period begins
9:50 AM	20	27	50		
10:10 AM	40	70	130		
10:30 AM	60	83	150		
10:40 AM	70	88	170		
10:50 AM	80	96	180		
11:00 AM	90	84	160		
11:10 AM	100	92	170		
11:20 AM	110	92	170		
11:30 AM	120	120	230		
11:40 AM	130	109	200		
11:50 AM	140	161	300		
12:00 NOON	150	150	280		
12:30 PM	180	148	275		
12:40 PM	190	157	290		
12:50 PM	200	157	290		
1:00 PM	210	170	320	40,200	End first rise
1:15 PM	225	280	520		Kneading
1:20 PM	230	282	530	49,000	Kneading
1:40 PM	250	290	540		Second rise period
1:50 PM	260	290	540		
2:00 PM	270	270	500		
2:10 PM	280	269	500		
2:30 PM	300	240	450		
2:40 PM	310	240	450	88,500	End second rise period
3:00 PM	330	60	5,800		Baking
3:10 PM	340	110	10,600		
3:20 PM	350	119	11,400		
3:30 PM	360	212	20,400		
3:40 PM	370	230	22,100	713,000	End baking

Ethanol E.R. = $C \cdot V \cdot C_1/0.28$ (see Appendix B)
C_1 = $16/24,500 = 6.53 \times 10^{-4}$
V = 800 cc/min (test)
V = 41,050 cc/min (oven)

NOVEMBER 15, 1977 BREADMAKING EXPERIMENT
SPONGE-DOUGH PROCESS

Time	Time elapsed (min)	Nonmethane organics: Concentration expressed as methane (ppm)	Nonmethane organics: Ethanol emission rate (µg/min)	Accumulated ethanol emissions (µg)	Comments
8:30 AM	0	0	0		First rise
10:00 AM	90	333	8		
10:10 AM	100	252	7		
10:20 AM	110	252	7		
11:00 AM	150	434	10		
11:10 AM	160	141	3		
11:20 AM	170	292	7		
11:30 AM	180	817	20		
11:40 AM	190	524	10		
11:50 AM	200	888	20		
12:00 NOON	210	746	20		
12:25 PM	235	646	15		
12:30 PM	240	1,049	25		
12:40 PM	250	1,341	30		
12:50 PM	260	1,452	35		
1:05 PM	275	1,473	35	3,200	
1:20 PM	290	555	13		Kneading
1:50 PM	320	424	10	4,000	Proofing
2:00 PM	330	605	15		
2:10 PM	340	585	13		
2:20 PM	350	575	13		
2:30 PM	360	444	10	4,500	
2:40 PM	370	272	17,500		In oven
2:50 PM	380	212	13,500		
3:00 PM	390	595	38,100		
3:10 PM	400	867	55,600	97,400	
3:20 PM	410	1,241	79,700		
3:30 PM	420	1,150	73,500		
3:40 PM	430	938	60,200		
3:50 PM	440	676	43,400		
4:00 PM	450	535	34,320		
4:10 PM	460	400	25,700		
4:20 PM	470	817	20	4,423,000	Out of oven
4:30 PM	480	1,130	25		In tent
4:40 PM	490	1,120	25		
4:50 PM	500	1,059	25		
5:00 PM	510	938	20		
5:10 PM	520	847	20	4,424,000	Ended

Ethanol E.R. = $C \cdot V \cdot C_1/0.28$ (see Appendix B)
C_1 = 16/24,500 = 6.53 x 10-4
V = 10 cc/min (tent)
V = 2.74×10^4 cc/min (oven)